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First principles study of U-Al system ground state

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Abstract

Formation energies of the binary intermetallic compounds UAl_n (n = 2, 3, 4) have been evaluated in the frame of the Density Functional Theory (DFT) using a pseudopotentials method implemented in the Vienna Ab-initio Simulation Package (VASP) code with spin polarized approximation and spin orbit coupling. As a side issue within this work, we analyzed the spin and orbital magnetic moments of uranium ions in the respective intermetallic compounds

Keywords: Intermetallic compounds; ab initio; uranium alloys; formation energies; magnetic moments.

1. Introduction

Nuclear Test and Research Reactors employ fuel elements where an uranium based alloy is dispersed in a aluminum based matrix. Under irradiation, an interface growths by interdiffusion between fuel and matrix that leads to swelling of the fuel element. In the case the fuel is an U-Mo alloy, the swelling is unacceptable for the thermo-hydraulic design of the nucleus of the reactor [Sears et al, 2006]. Consequently, research effort is

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focused on reaction products and theirs growth kinetics. Recently published data report that the reaction products are UAl_3, UAl_4, UMo_2Al_{20} and $U_6Mo_4Al_{43}$ [Mazaudier et al, 2008, and references therein]. However, growth kinetics and global activation energy are similar for U-Mo/Al and U/Al diffusion couples though in this last case the interface contains only UAl_3 and UAl_4 phases. It comes out that the influence of Mo ternary addition can be neglected for the evaluation of the growth of the reactions products and theirs activation energies [Palancher et al, 2007].

In previous works we have presented our simulations of the growth kinetics of the UAl_4 compound in UAl_3/Al diffusion couples through a CalPhad model of the thermodynamic properties and atomic mobilities [Kniznik et al, 2011].

Activation energy for diffusion of the pure elements in the intermetallic phases is the key parameter needed for those simulations, but unfortunately there is no experimental information on them. So, we are determined to calculate them using quantum chemical computational methods based on the Functional Density Theory [Hohenberg and Kohn, 1964; Kohn and Sham, 1965].

In order to obtain reliable data for defects formation and migration energies it is necessary to introduce in the single particle Hamiltonian the interactions needed to reproduce the properties of the pure metals as well as of the three intermetallic compounds in the U-Al system. As a first approach, we used the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method in the Generalized Gradient Approximation (GGA) for the exchange and correlation functional, including relativistic corrections, as it is implemented in the WIEN2K code [Blaha et al, 2001]. In this frame, we calculated lattice parameters, bulk elastic moduli and total energies for the pure elements and the intermetallic compounds [Pizarro et al, 2008], for the subsequent calculation of the UAl_4 formation energy containing constitutional uranium vacancies [Alonso et al, 2009]. However, the use of an all-electron method as the WIEN2K code implies a limitation in the size of the supercell, which results not sufficiently large to avoid defect-defect interactions due to the periodicity of the supercell. To solve this problem it is recommended to use a pseudopotentials method as it is implemented in the Vienna Ab-initio Simulation Package (VASP) [Kresse et al, 1993, 1993, 1996, 1996]. With this aim, we analyzed our results on the U-Al system obtained with the WIEN2K code using in this work the VASP code including magnetic effects through the spin polarized (SP) and spin-orbit coupling (SOC) interaction terms. In the following sections, we present and discuss our results.

2. Computational methods

All calculations in this work were performed in the framework of the DFT as implemented in VASP code.

For the exchange-correlation interaction the Perdew, Burke and Ernzerhof (PBE) GGA approximation was used [Perdew et al, 1996]. The ion-electron interaction was described by PAW pseudopotentials [Vanderbilt, 1990; Kresse and Hafner, 1994] with valence electron configurations of U and Al $6s^26p^65f^36d^17s^2$ and y $3s^23p^1$ respectively.

The total energy for each phase was calculated for three cases: spin polarized (SP), non spin polarized (NSP), and finally including spin-orbit coupling (SP + SOC) [Andersen, 1975].

The plane-wave cutoff energy used was 600 eV. To calculate the total energy, the integration of the Brillouin zone was performed using the tetrahedron method with Blöchl corrections [Blöchl et al, 1994]. For structure relaxation, we used the Methfessel-Paxton method of order 2 [Methfessel and Paxton, 1989] and a conjugate-gradient scheme until the forces acting on the atoms are less than 0.01 eV/Å. The convergence criterion for the self-consistent cycle was set to 10^{-4} eV in the total energy of each system. The k-point meshes for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme [Monkhorst and Pack, 1976]. In all the structures the calculations were performed with a $9 \times 9 \times 9$ k-points grid.

For each phase, we relaxed the structure and then calculated the total energy for cell volumes around the experimental value. The total energy was plotted as a function of cell volume and the resulting curve was

fitted using the Birch-Murnaghan equation of state [Birch, 1947] to determine the equilibrium volume (and hence the equilibrium lattice parameter) and the bulk moduli.

The same steps and same parameters were used for calculating properties of αU, UAl_2, UAl_3, UAl_4 and Al, in order to cancel any systematic error in energy differences.

The total energies obtained were used to calculate the energy of formation of the three intermetallic compounds. The energy of formation of compound UAl_n is calculated as:

$$\Delta E_f(UAl_n) = E_T(UAl_n) - \frac{1}{n+1} E_T(U) - \frac{n}{n+1} E_T(Al) \quad (1)$$

3. Results and discussion

SP electronic structure calculations for total energy of pure elements and intermediate phases show that the most stable structures are paramagnetic (PM) for αU and Al, ferromagnetic (FM) for UAl_2 and UAl_3, and antiferromagnetic (AFM) for UAl_4. The experimental results of specific heat, magnetic susceptibility and electrical resistivity at low temperature of the three intermediate phases [Burzo et al, 1989, 1995; Lupsa et al, 1994], clearly indicate a magnetic behavior consistent with the spin fluctuations model [Moriya, 1979]. The FM character of the system with spin fluctuation was observed in UAl_2 [De Boer, 1982] but not in the other two compounds. Table 1 shows the calculated spin magnetic moment of uranium in each compound. There is some uniformity in its value as the distance between U ions in compounds increases, but this result is also observed in the experimental values of effective magnetic moment in the paramagnetic state. The lower value of the calculated spin moment is consistent with the itinerant nature of 5f electrons of uranium captured by the SP calculation.

The inclusion of spin-orbit coupling in SP electronic structure calculations results in spin and orbital magnetic moments of uranium that are in opposite directions, according to Hund's third law. It can also be observed an increasing tendency of the orbital momentum module as the distance between U ions grows, confirming that the crystal field buffers the orbital momentum of uranium 5f electrons. Finally, the total magnetic moment is very small for UAl_2 y UAl_3, confirming that spin-orbit and crystal field interactions are of similar magnitude in these compounds.

Table 1. Magnetic moment of uranium ions (μ_B).

μ	αU	UAl_2	UAl_3	UAl_4
μ_{eff}	-	3.14	3.7	3.9
μ_{espin} (SP)	0.00	2.21	2.10	2.10
μ_{espin} (SP+SOC)	0.07	1.97	1.88	1.78
$\mu_{orbital}$ SP+SOC)	0.14	-1.78	-2.04	-2.15
μ_{total} (SP+SOC)	0.21	0.19	0.16	0.37

In the preceding analysis we have ignored the results of αU because there is a violation of Hund's third law when including spin-orbit coupling. However, the calculation was verified and there is a previous mention in literature [Hjelm, 1993].

The easy magnetization directions found during calculations (SP + SOC) were [0 1 0] for αU and [0 0 1] for all compounds.

Table 2 shows the total energy per atom for pure elements and intermediate phases of U-Al system for all types of calculation (NSP, SP and SP+SOC). Table 3 presents the results obtained for the lattice parameters

and bulk elastic moduli calculations (SP+ SOC). Lattice parameters do not differ by more than 2% from experimental value and the agreement is also good for the bulk elastic modulus of the pure elements. For the bulk moduli of the intermediate phases the agreement is poor in the case of UAl_3 and UAl_4 but the experimental data reported are unique in the literature.

Table 2. Total energy per atom for pure elements and intermediate phases of U-Al system (eV).

	E_T (NSP)	E_T (SP)	E_T (SP+SOC)
U	-11.292	-11.293	-14.307
UAl_2	-6.372	-6.411	-7.438
UAl_3	-5.720	-5.749	-6.526
UAl_4	-5.332	-5.364	-5.989
Al	-3.727	-3.727	-3.726

Table 3. Lattice parameters and Bulk moduli (B_0) for pure elements and intermediate phases of U-Al system.

	Structure		Lattice parameter (Å)		B_0 (GPa)	
	Pearson Strukturbericht Space Group		calculated	experimental	calculated	experimental
αU	oC4	a	2.7898	2.8444 [Barrett, 1963]	135	135.5 [Yoo et al, 1998]
	A20	b	5.8782	5.8669		
	Cmcm (63)	c	4.8723	4.9316		
		y	0.0973	0.102		
UAl_2	cF24	a	7.6290	7.74 [Kassner et al, 1989]	93	83± 9 [Sahu et al, 2000]
	C15					
	$Fd\bar{3}m$					
UAl_3	cP4	a	4.23739	4.26 [Kassner et al, 1989]	90	70 ± 6 [Sahu et al, 2000]
	$L1_2$					
	$Pm\bar{3}m$					
UAl_4	oI20	a	4.3515	4.397 [Runnals and Boucher, 1965]	88	73 ±5 [Sahu et al, 2000]
	$D1_b$	b	6.1826	6.251		
	Imma	c	13.6992	13.714		
Al	cF4	a	4.0470	4.0496 [Kassner et al, 1989]	73	72.2 [Kittel, 1996]
	$Fm\bar{3}m$					

Figure 1 shows the energies of formation for the ground state of U-Al system obtained from the data in Table 2. It is observed that UAl_3 compound is slightly metastable in any calculation method; this result for (SP+SOC) calculation, was previously reported by Sedmidubsky et al [Sedmidubsky et al, 2010] with

WIEN2K code. The influence on the stabilities of the intermediate phases of each interaction included in the single-particle Hamiltonian is illustrated in fig 1.

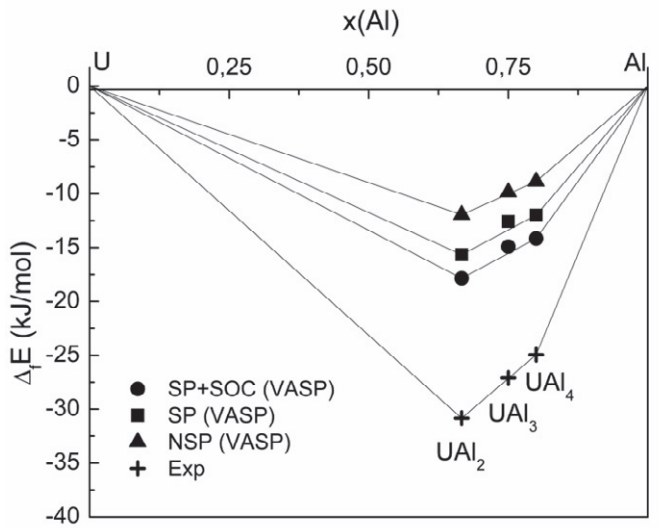

Fig. 1. Energies of formation for U-Al system. Calculated: spin polarized (SP), Non Spin Polarized (NSP), and SP with Spin Orbit Coupling (SOC). Reference for experimental data: Kassner et al, 1989.

4. Conclusions

Although the inclusion of the spin-orbit coupling term has a significant effect on the formation energies values, the agreement with experimental data is still poor. To our opinion, compounds formation energies are greatly affected by the value of total energy for αU, and a further insight is needed to study the observed anomaly that violates the third Hund rule when SOC effect is included.

However, and besides the mentioned discrepancies, the present results offer a view of the cohesive characteristics related to magnetic effects for the UAl_n compounds.

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